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(54)【発明の名称】ペロブスカイト型複合酸化物の製造方法

(57)【要約】

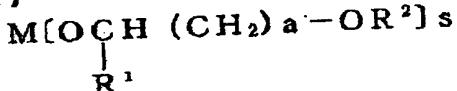
【目的】貴金属元素をペロブスカイト型構造の結晶格子中に入れることによって貴金属元素の分散度を増加させ、触媒活性等の特性を向上させる。

【構成】La、Ce、Fe及びCoのアルコキシアルコラートに有機溶媒としてトルエンを加えて攪拌し溶解させて混合アルコキシアルコラート溶液としたものに、硝酸パラジウム水溶液を徐々に滴下し、沈澱を生成させる。その溶液を室温下で攪拌した後、減圧下でトルエンと水を反応系外に留去し、黒褐色のLa_{0.9}Ce_{0.1}Fe_{0.9}P_{0.05}O₄酸化物の前駆体を得た。この前駆体の粘稠物を通風乾燥した後、空気中で電気炉で600°Cで2時間熱処理してペロブスカイト型単一結晶相のLa_{0.9}Ce_{0.1}Fe_{0.9}_{0.57}Co_{0.38}Pd_{0.05}O₄粉末を得た。

【特許請求の範囲】

【請求項1】 $(A_1, A')_x (B_1, B')_y O_3$ (式中、 A は La , Nd 及び Pr のうちの少なくとも1種、 A' は Ce , Mg , Ca , Sr , Ba 及び Y のうちの少なくとも1種、 B は Co , Mn , Fe , Ni , Cr , Cu 及び Zn のうちの少なくとも1種、 B' は Ru , Rh , Pd , Os , Ir 及び Pt からなる貴金属元素のうちの少なくとも1種、 $0 < x < 0.9$, $0.01 < y < 0.2$ である) で示されるペロブスカイト型複合酸化物を構成する金属元素のうち、 貵金属元素 B' を除く金属元素の下記式で示される金属アルコキシアルコラートを有機溶媒に溶解して混合アルコキシアルコラート溶液としたものを、 前記ペロブスカイト型複合酸化物を構成する貴金属元素 B' の塩の水溶液により加水分解した後、 有機溶媒及び水分を除去して前記ペロブスカイト型複合酸化物の前駆体を形成する工程と、 前記前駆体を酸化雰囲気中、 $500 \sim 800^\circ C$ で焼成してペロブスカイト型複合酸化物とする工程と、 を含むペロブスカイト型複合酸化物の製造方法。

【化1】



(式中、 M は前記 A , A' 及び B のうちのいずれかの金属、 R' は水素原子又は低級アルキル基、 R^1 は低級アルキル基、 a は $1 \sim 3$ の整数、 s は $2 \sim 3$ の整数をそれぞれ示す。)

【請求項2】 前記金属アルコキシアルコラートは金属メトキシアルコラートと金属エトキシアルコラートのうちのいずれかである請求項1に記載のペロブスカイト型複合酸化物の製造方法。

【請求項3】 前記金属メトキシアルコラートと金属エトキシアルコラートはエチレートとプロピレートのうちのいずれかである請求項2に記載のペロブスカイト型複合酸化物の製造方法。

【請求項4】 前記有機溶媒はハイドロカーボン類、 アルコール類、 ケトン類及びエステル類のいずれかである請求項1～3のいずれかに記載のペロブスカイト型複合酸化物の製造方法。

【請求項5】 前記有機溶媒はキシレン、 トルエン及びベンゼンのうちのいずれかである請求項4に記載のペロブスカイト型複合酸化物の製造方法。

【請求項6】 前記貴金属元素 B' の塩の水溶液は硝酸塩、 塩化物、 ジニトロジアンミン硝酸塩、 ヘキサアンミン塩化物、 ヘキサクロロ酸水和物及びシアノ化カリウム塩のうちのいずれかである請求項1～5のいずれかに記載のペロブスカイト型複合酸化物の製造方法。

【請求項7】 前駆体からペロブスカイト型複合酸化物を得る焼成温度が $500 \sim 600^\circ C$ である請求項1～6のいずれかに記載のペロブスカイト型複合酸化物の製造

方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は一酸化炭素 (CO) 、 炭化水素 (HC) 及び酸化窒素 (NO_x) の浄化能力に優れ、 排気ガス浄化用触媒や天然ガスなどの燃焼用触媒などとして利用されるペロブスカイト型複合酸化物を製造する方法に関するものである。

【0002】

【従来の技術】 排気ガス浄化用三元触媒としてはアルミニナ担体に Pt , Rh , Pd などの貴金属を担持した貴金属触媒が実用化されて広く使用されている。また、 希土類金属、 アルカリ土類金属及び遷移金属から構成されるペロブスカイト型構造を有する複合酸化物に貴金属を共存させた触媒は、 CO , HC 及び NO_x を浄化する安価な排気ガス浄化用三元触媒として実用化が期待されている(特開昭59-87046号公報、 特開昭60-82138号公報、 特開平1-168343号公報参照)。

【0003】 これらの触媒では微細なペロブスカイト型複合酸化物表面に Pd などの貴金属が分散された状態で担持されている。しかし、 貴金属元素がペロブスカイト型複合酸化物の表面に担持された状態では、 高温で使用され続けている間に貴金属元素が凝集体となり、 貴金属元素の分散度が小さくなつて触媒活性等の特性が劣化しやすい。

【0004】 そこで、 貴金属元素の分散度を増加させて触媒活性等を向上させるために、 貴金属元素をペロブスカイト型構造の結晶格子中に取り込む方法が提案されている。その1つの方法として、 貴金属元素を含むペロブスカイト型複合酸化物を構成する金属元素の塩とクエン酸とを溶解した水溶液を調製し、 その水溶液を乾燥させることにより金属元素とクエン酸との錯体を形成した後、 その錯体を真空中又は不活性ガス中で $350^\circ C$ 以上に加熱して仮焼成体を形成し、 それを酸化雰囲気中で焼成することによりペロブスカイト型複合酸化物を形成する(特開平6-100319号公報参照)。

【0005】

【発明が解決しようとする課題】 本願発明は特開平6-100319号公報で提案された方法と同じく、 貴金属元素をペロブスカイト型構造の結晶格子に入れることによって貴金属元素の分散度を増加させ、 触媒活性等の特性を向上させるためのものであるが、 その方法とは異なる別の方法を提供することを目的とするものである。

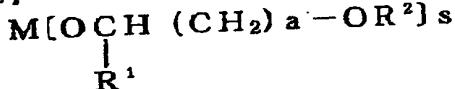
【0006】

【課題を解決するための手段】 本発明の製造方法は、 $(A_1, A')_x (B_1, B')_y O_3$ (式中、 A は La , Nd 及び Pr のうちの少なくとも1種、 A' は Ce , Mg , Ca , Sr , Ba 及び Y のうちの少なくとも1種、 B は Co , Mn , Fe , Ni , Cr , Cu 及び Zn のうちの少なくとも1種、 B' は Ru , Rh , Pd , Os , Ir 及び

Ptからなる貴金属元素のうちの少なくとも1種、 $0 < x < 0.9$ 、 $0.01 < y < 0.2$ である)で示されるペロブスカイト型複合酸化物を構成する金属元素のうち、貴金属元素B'を除く金属元素の金属アルコキシアルコラートを有機溶媒に溶解して混合アルコキシアルコラート溶液としたものを、ペロブスカイト型複合酸化物を構成する貴金属元素B'の塩の水溶液により加水分解した後、有機溶媒及び水分を除去してペロブスカイト型複合酸化物の前駆体を形成する工程と、その前駆体を酸化雰囲気中、 $500\sim800^\circ\text{C}$ 、好ましくは $500\sim600^\circ\text{C}$ で焼成してペロブスカイト型複合酸化物とする工程とを含んでいる。

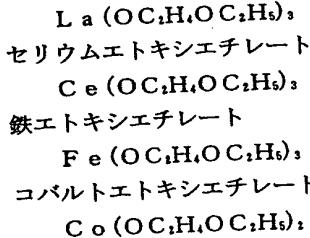
【0007】金属アルコキシアルコラートとしては下記式で示される化合物を用いることができる。

【化2】



(式中、Mは上記のA、A'及びBのうちのいずれかの金属、R'は水素原子又は低級アルキル基、R'1は低級アルキル基、aは1~3の整数、sは2~3の整数をそれぞれ示す。) 金属アルコキシアルコラートは、その中でも金属メトキシアルコラートと金属エトキシアルコラートのうちのいずれかであることが好ましく、その金属メトキシアルコラートと金属エトキシアルコラートはエチレートとプロピレートのうちのいずれかであることが好ましい。

【0008】また、有機溶媒としては、金属アルコキシアルコラート類を溶解し得るものであれば特に限定されランタンエトキシエチレート



これらの金属アルコキシアルコラートを 500mL 容量の丸底フラスコに入れ、有機溶媒としてトルエン 200mL を加えて攪拌し、溶解させて混合アルコキシアルコラート溶液とした。

【0011】一方、貴金属塩の水溶液として硝酸パラジウム溶液(Pd分4.4wt%) 12.1g (Pd換算で 0.53g 、 0.005モル に相当)に脱イオン水 100mL を加えた水溶液を調製した。この硝酸パラジウム水溶液を先の混合アルコキシアルコラート溶液中に室温下で約15分間かけて徐々に滴下した。硝酸パラジウム水溶液の滴下により直ちに褐色の沈殿が生成し、次第に粘稠となる。その溶液を室温下で2時間攪拌した後、減圧※ランタンエトキシエチレート

*することなく用いることができる。そのような有機溶媒として、具体的には例えばハイドロカーボン類、アルコール類、ケトン類、エステル類などが挙げられ、溶解性や操作性を考慮すると、キシレン、トルエン、ベンゼンなどの芳香族炭化水素類が好ましく用いられる。貴金属元素B'の塩の水溶液は硝酸塩、塩化物、ジニトロジアンミン硝酸塩、ヘキサアンミン塩化物、ヘキサクロロ酸水和物及びシアン化カリウム塩のうちのいずれかであることが好ましいが、それに限定されるものではない。

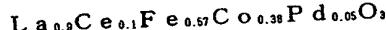
【0009】

【作用】貴金属元素はアルコキシアルコラートにするのが困難であるため水溶性の塩として水溶液にし、他の金属元素はアルコキシアルコラートとして有機溶媒に溶解させる。両者を混合し攪拌し有機溶媒と水分を除去すると、ペロブスカイト型複合酸化物を構成する金属元素が均一に混合した前駆体となる。その前駆体を大気などの酸化雰囲気中で焼成することにより、貴金属が結晶格子に取り込まれたペロブスカイト型複合酸化物が得られる。ペロブスカイト型複合酸化物結晶を形成するために 500°C 以上で焼成することが必要である。本発明の製造方法では 600°C 以下でも焼成が可能である。焼成温度を $500\sim600^\circ\text{C}$ と低くすれば、製造設備の面からも有利となる。

【0010】

【実施例】

(実施例1)



貴金属元素以外の金属元素のアルコキシアルコラートとして次のものを用意する。

36.6 g (0.09モル)

4.1 g (0.01モル)

18.4 g (0.057モル)

9.0 g (0.038モル)

※下で水分と有機溶媒のトルエンとを反応系外に留去し、黒褐色の La Ce Fe Co Pd 酸化物の前駆体を得た。

【0012】この前駆体の粘稠物をシャーレに移し、 60°C で24時間通風乾燥した後、空気中、電気炉で 600°C で2時間熱処理して黒褐色の粉末を得た。その粉末は図1に示される粉末X線回折の結果から、 $\text{La}_{0.9}\text{Ce}_{0.1}\text{Fe}_{0.57}\text{Co}_{0.33}\text{Pd}_{0.05}\text{O}_3$ のペロブスカイト型単一結晶相であり、比表面積は $30\text{ m}^2/\text{g}$ であった。

【0013】(実施例2)



貴金属元素以外の金属元素のアルコキシアルコラートとして次のものを用意する。

36.6 g (0.09モル)

$\text{La}(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_5)_3$
 セリウムエトキシエチレート
 $\text{Ce}(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_5)_3$
 マンガンエトキシエチレート
 $\text{Mn}(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_5)_3$
 コバルトエトキシエチレート
 $\text{Co}(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_5)_3$

これらの金属アルコキシアルコラートを500mI容量の丸底フラスコに入れ、有機溶媒としてキシレン200mIを加えて攪拌し、溶解させて混合アルコキシアルコラート溶液とした。

【0014】実施例1と同様に、貴金属塩の水溶液として硝酸パラジウム溶液(Pd分4.4wt%)12.1g(Pd換算で0.53g、0.005モルに相当)に脱イオン水100mIを加えた水溶液を調製した。この混合アルコキシアルコラート溶液と硝酸パラジウム水溶液とから実施例1と同じ方法により黒褐色の LaCeMnC *

ネオジムエトキシエチレート
 $\text{Nd}(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_5)_3$
 カルシウムエトキシエチレート
 $\text{Ca}(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_5)_3$
 鉄エトキシエチレート
 $\text{Fe}(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_5)_3$
 マンガンエトキシエチレート
 $\text{Mn}(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_5)_3$

実施例1と同様に、これらの金属アルコキシアルコラートを500mI容量の丸底フラスコに入れ、有機溶媒としてトルエン200mIを加えて攪拌し、溶解させて混合アルコキシアルコラート溶液とした。

【0016】貴金属塩の水溶液として硝酸パラジウム溶液(Pd分4.4wt%)29.0g(Pd換算で1.27g、0.012モルに相当)に脱イオン水100mIを加えた水溶液を調製した。この混合アルコキシアルコラート溶液と硝酸パラジウム水溶液とから実施例1と同じ方法により黒褐色の NdCaFeMnPd 酸化物の前駆体を得、それを実施例1と同じ条件で熱処理して黒褐色の粉末を得た。その粉末は $\text{Nd}_{0.8}\text{Ca}_{0.4}\text{Fe}_{0.52}\text{Mn}_{0.38}\text{Pd}_{0.12}\text{O}_3$ のペロブスカイト型単一結晶相であり、比表面積は36m²/gであった。

* o P d 酸化物の前駆体を得、それを実施例1と同じ条件で熱処理して黒褐色の粉末を得た。その粉末は図2に示される粉末X線回折の結果から、 $\text{La}_{0.9}\text{Ce}_{0.1}\text{Mn}_{0.57}\text{Co}_{0.38}\text{Pd}_{0.05}\text{O}_3$ のペロブスカイト型単一結晶相であり、比表面積は36m²/gであった。

【0015】(実施例3)

$\text{Nd}_{0.8}\text{Ca}_{0.4}\text{Fe}_{0.52}\text{Mn}_{0.38}\text{Pd}_{0.12}\text{O}_3$

貴金属元素以外の金属元素のアルコキシアルコラートとして次のものを用意する。

24.7g(0.06モル)

8.7g(0.04モル)

16.8g(0.052モル)

8.4g(0.036モル)

※同じ方法により黒褐色の NdCaFeMnPd 酸化物の前駆体を得、それを実施例1と同じ条件で熱処理して黒褐色の粉末を得た。その粉末は $\text{Nd}_{0.8}\text{Ca}_{0.4}\text{Fe}_{0.52}\text{Mn}_{0.38}\text{Pd}_{0.12}\text{O}_3$ のペロブスカイト型単一結晶相であり、比表面積は32m²/gであった。

【0017】(実施例4)

$\text{Pr}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Pd}_{0.1}\text{O}_3$

貴金属元素以外の金属元素のアルコキシアルコラートとして次のものを用意する。

29.3g(0.08モル)

4.8g(0.02モル)

18.5g(0.09モル)

★褐色の PrSrMnPd 酸化物の前駆体を得、それを実施例1と同じ条件で熱処理して黒褐色の粉末を得た。その粉末は $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Pd}_{0.1}\text{O}_3$ のペロブスカイト型単一結晶相であり、比表面積は29m²/gであった。

【0020】(実施例5)

$\text{La}_{0.2}\text{Ba}_{0.7}\text{Y}_{0.1}\text{Cu}_{0.48}\text{Cr}_{0.48}\text{Pt}_{0.04}\text{O}_3$

貴金属元素以外の金属元素のアルコキシアルコラートとして次のものを用意する。

【0018】実施例1と同様に、これらの金属アルコキシアルコラートを500mI容量の丸底フラスコに入れ、有機溶媒としてトルエン200mIを加えて攪拌し、溶解させて混合アルコキシアルコラート溶液とした。貴金属塩の水溶液として硝酸パラジウム溶液(Pd分4.4wt%)24.2g(Pd換算で1.06g、0.01モルに相当)に脱イオン水100mIを加えた水溶液を調製した。

【0019】この混合アルコキシアルコラート溶液と硝酸パラジウム水溶液とから実施例1と同じ方法により黒★50

7 ランタンエトキシエチレート $\text{La}(\text{OC}_2\text{H}_4\text{O C}_2\text{H}_5)_3$	8.1 g (0.02モル)
バリウムエトキシエチレート $\text{Ba}(\text{OC}_2\text{H}_4\text{O C}_2\text{H}_5)_2$	22.1 g (0.07モル)
イットリウムエトキシエチレート $\text{Y}(\text{OC}_2\text{H}_4\text{O C}_2\text{H}_5)_3$	3.6 g (0.01モル)
銅エトキシエチレート $\text{Cu}(\text{OC}_2\text{H}_4\text{O C}_2\text{H}_5)_2$	11.6 g (0.048モル)
クロムエトキシエチレート $\text{Cr}(\text{OC}_2\text{H}_4\text{O C}_2\text{H}_5)_3$	15.3 g (0.048モル)

【0021】実施例1と同様に、これらの金属アルコキシアルコラートを500ml容量の丸底フラスコに入れ、有機溶媒としてトルエン200mlを加えて攪拌し、溶解させて混合アルコキシアルコラート溶液とした。貴金属塩の水溶液としてジニトロジアンミン白金硝酸溶液 (Pt分8.5wt%) 9.2g (Pt換算で0.78g、0.004モルに相当) に脱イオン水100mlを加えた水溶液を調製した。

【0022】この混合アルコキシアルコラート溶液と白金塩水溶液とから実施例1と同じ方法により黒褐色のL*20

ランタン-1-メトキシ-2-プロピレート $\text{La}(\text{OCH}(\text{CH}_3)\text{CH}_2\text{OCH}_3)_3$	32.5 g (0.08モル)
バリウム-1-メトキシ-2-プロピレート $\text{Ba}(\text{OCH}(\text{CH}_3)\text{CH}_2\text{OCH}_3)_2$	6.3 g (0.02モル)
ニッケル-1-メトキシ-2-プロピレート $\text{Ni}(\text{OCH}(\text{CH}_3)\text{CH}_2\text{OCH}_3)_2$	11.4 g (0.048モル)
コバルト-1-メトキシ-2-プロピレート $\text{Co}(\text{OCH}(\text{CH}_3)\text{CH}_2\text{OCH}_3)_2$	11.9 g (0.050モル)

【0024】実施例1と同様に、これらの金属アルコキシアルコラートを500ml容量の丸底フラスコに入れ、有機溶媒としてトルエン200mlを加えて攪拌し、溶解させて混合アルコキシアルコラート溶液とした。貴金属塩の水溶液として硝酸ロジウム溶液 (Rh分4.478wt%) 4.69g (Rh換算で0.21g、0.002モルに相当) に脱イオン水100mlをえた水溶液を調製した。

【0025】この混合アルコキシアルコラート溶液と硝酸ロジウム水溶液とから実施例1と同じ方法により黒褐色

ランタンエトキシエチレート $\text{La}(\text{OC}_2\text{H}_4\text{O C}_2\text{H}_5)_3$	36.6 g (0.09モル)
セリウムエトキシエチレート $\text{Ce}(\text{OC}_2\text{H}_4\text{O C}_2\text{H}_5)_3$	4.1 g (0.01モル)
コバルトエトキシエチレート $\text{Co}(\text{OC}_2\text{H}_4\text{O C}_2\text{H}_5)_2$	21.3 g (0.09モル)

【0027】実施例1と同様に、これらの金属アルコキシアルコラートを500ml容量の丸底フラスコに入れ、有機溶媒としてトルエン200mlを加えて攪拌し、溶解させて混合アルコキシアルコラート溶液とした。貴金属塩の水溶液としてジニトロジアンミン白金硝酸溶液 (Pt分8.5wt%) 11.5g (Pt換算で

* a Ba Y Cu Cr Pt 酸化物の前駆体を得、それを実施例1と同じ条件で熱処理して黒褐色の粉末を得た。その粉末は $\text{La}_{0.1}\text{Ba}_{0.7}\text{Y}_{0.1}\text{Cu}_{0.48}\text{Cr}_{0.48}\text{Pt}_{0.04}\text{O}_x$ のペロブスカイト型単一結晶相であり、比表面積は $2.6 \text{ m}^2/\text{g}$ であった。

【0023】(実施例6)

$\text{La}_{0.8}\text{Ba}_{0.1}\text{Ni}_{0.48}\text{Co}_{0.50}\text{Rh}_{0.02}\text{O}_3$
貴金属元素以外の金属元素のアルコキシアルコラートとして次のものを用意する。

※色の La Ba Ni Co Rh 酸化物の前駆体を得、それを30 実施例1と同じ条件で熱処理して黒褐色の粉末を得た。その粉末は $\text{La}_{0.8}\text{Ba}_{0.1}\text{Ni}_{0.48}\text{Co}_{0.50}\text{Rh}_{0.02}\text{O}_3$ のペロブスカイト型単一結晶相であり、比表面積は $2.7 \text{ m}^2/\text{g}$ であった。

【0026】(実施例7)

$\text{La}_{0.9}\text{Ce}_{0.1}\text{Co}_{0.00}\text{Pt}_{0.05}\text{Ru}_{0.05}\text{O}_3$
貴金属元素以外の金属元素のアルコキシアルコラートとして次のものを用意する。

36.6 g (0.09モル)

4.1 g (0.01モル)

21.3 g (0.09モル)

0.98g、0.005モルに相当) 及び硝酸ルテニウム溶液 (Ru分3.930wt%) 13.0g (Ru換算で0.51g、0.005モルに相当) に脱イオン水100mlをえた水溶液を調製した。

【0028】この混合アルコキシアルコラート溶液と白金塩及びルテニウム塩の混合水溶液とから実施例1と同

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【0037】(耐久試験) 下記のリッチガスとリーンガスを5秒毎に切り換えて900°Cで30分、750°Cで30分のサイクルを50回(50時間)繰り返して耐久*

* 試験を行なった。触媒を通るガス流の空間速度(SV)は30,000/時間とした。

	リッチガス	リーンガス
CO	2.6%	0.7%
HC(C ₁ 換算濃度)	0.19%	0.19%
H ₂	0.87%	0.23%
CO ₂	8%	8%
NO	0.17%	0.17%
O ₂	0.74%	1.89%
H ₂ O蒸気	10%	10%
N ₂	残部	残部

HCの内訳は、C₃H₈が0.15%、C₂H₆が0.04%であった。

【0039】(触媒活性の評価) 上記のリッチガスとリーンガスを1秒毎に切り換えるながら、テスト用ハニカムサンプルに流し、ガスを加熱し昇温していく。昇温速度は20°C/分とし、触媒入口付近のガス温を測定し制

【0038】

	リッチガス	リーンガス
CO	2.6%	0.7%
HC(C ₁ 換算濃度)	0.19%	0.19%
H ₂	0.87%	0.23%
CO ₂	8%	8%
NO	0.17%	0.17%
O ₂	0.74%	1.89%
H ₂ O蒸気	10%	10%
N ₂	残部	残部

※御した。触媒活性の測定は耐久試験の前と後とで行なつた。触媒を通るガス流の空間速度(SV)は30,000/時間とした。350°CにおけるHCとCOの浄化率(%)を表1にまとめて示す。

【0040】

【表1】

	HC		CO	
	初期	耐久試験	初期	耐久試験後
実施例1	97	94	98	98
実施例2	99	97	99	98
実施例3	96	96	97	96
実施例4	97	96	97	97
実施例5	80	78	84	84
実施例6	91	88	96	94
実施例7	99	91	99	99
比較例a	82	63	91	89
比較例b	76	48	93	82
比較例c	83	67	96	92

【0041】HCに対する触媒活性は、初期状態においても耐久後においても比較例よりも実施例の方が優れています。COについては大幅な差は見られない。また、初期状態と耐久後のHCとCOの浄化率を比較すると、実施例での劣化は少なく、比較例での劣化は特にHCで大きく現れている。このように、耐久性においても本発明の方法による触媒は比較例のものよりも優れている。

【0042】窒素酸化物NO_xに対するテスト結果を示していないが、これはNO_xの浄化率は製造方法よりも貴金属元素の種類に大きく依存するためである。貴金属元素としてパラジウムを用いる場合にNO_xの浄化率が最も優れた結果になる。この発明によるペロブスカイト型複合酸化物はNO_xに対しても有効なものであり、三元触媒として作用するものである。

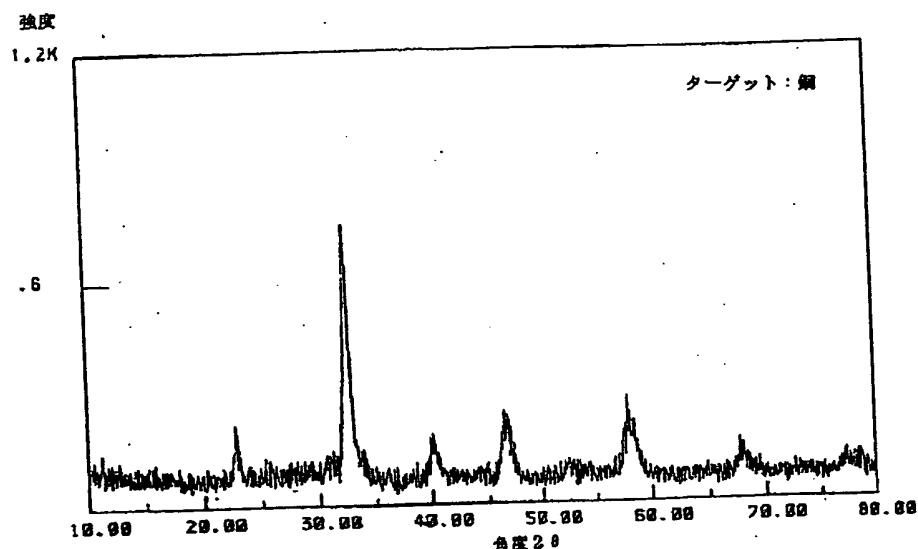
【0043】

【発明の効果】本発明の方法で製造したペロブスカイト型複合酸化物は、貴金属元素が結晶格子に入り、触媒活性が優れ、耐久性も優れた触媒となる。

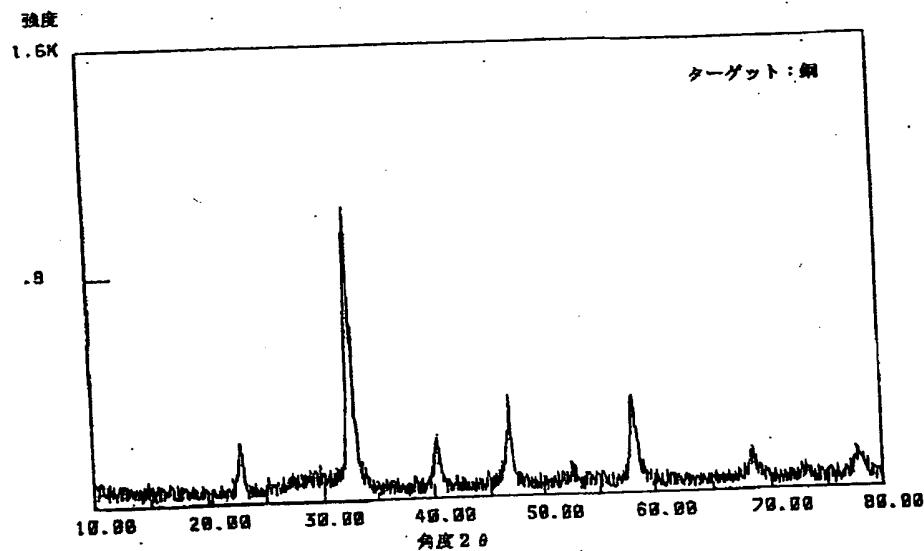
【図面の簡単な説明】

*

【図1】



【図2】



フロントページの続き

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 HOKKO CHEM IND CO LTD

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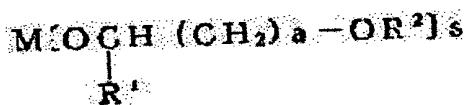
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(54) PRODUCTION OF PEROVSKITE TYPE COMPOUND OXIDE

(57)Abstract:

PURPOSE: To obtain a perovskite compound oxide, containing a noble metallic element introduced into a crystal lattice and excellent in catalyst activities and durability by adopting a specific method in obtaining the subject prescribed compound oxide containing the noble metallic element.

CONSTITUTION: This method is to provide the subject compound oxide represented by the formula, $(A_1-xA'_x)(B_1-yB'_y)O_3$ [A is at least one of La, Nd and Pr; A' is at least one of Ce, Mg, Ca, Sr, Ba and Y; B is at least one of Co, Mn, Fe, Ni, Cr, Cu and Zn; B' is at least one noble metallic element comprising Ru, Rh, Pd, Os, Ir and Pt; (x) is 0-0.9; (y) is 0.01-0.2]. In the method, an aqueous solution of a salt of B' is added to a solution prepared by dissolving a metallic alkoxyalcoholate represented by the formula [M is A, A' or B; R₂ is a lower alkyl; R₁ is H or R₂; (a) is 1-3; (s) is 2-3] of a metallic element except B' in an organic solvent and the metallic alkoxyalcoholate is hydrolyzed. The organic solvent and water are then removed to form a precursor of the compound oxide. The resultant precursor is then baked at 500-800°C in an oxidizing atmosphere.



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JAPANESE [JP,08-217461,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS
OPERATION EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

* NOTICES *

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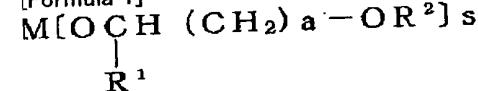
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] $(A_1-xA'_x)O_3(B_1-yB'_y)$ (among a formula at least one sort of A of La, Nd, and the Pr) A' At least one sort in Ce, Mg, calcium, Sr, Ba, and Y, B — Co, Mn, Fe, nickel, Cr, Cu, and Zn — inner at least one sort At least one sort in the noble-metals element with which B' consists of Ru, Rh, Pd, Os, Ir, and Pt, $0 < x < 0.9$ and $0.01 < y < 0.2$ — it is — among the metallic elements which constitute the perovskite mold multiple oxide shown What dissolved the metal alkoxy alcoholate shown by the following formula of the metallic element except noble-metals element B' in the organic solvent, and was used as the mixed alkoxy alcoholate solution The process which removes an organic solvent and moisture and forms the precursor of said perovskite mold multiple oxide after hydrolyzing with the water solution of the salt of noble-metals element B' which constitutes said perovskite mold multiple oxide, The manufacture approach of a perovskite mold multiple oxide including the process which calcinates said precursor at 500-800 degrees C among an oxidizing atmosphere, and is used as a perovskite mold multiple oxide.

[Formula 1]



(Among a formula, in a hydrogen atom or a low-grade alkyl group, and R2, a low-grade alkyl group and a show the integer of 1-3, and, as for M, s shows [the metal of the said A, A', or the B and R1] the integer of 2-3, respectively.)

[Claim 2] Said metal alkoxy alcoholate is the manufacture approach of the perovskite mold multiple oxide according to claim 1 which are either a metal methoxy alcoholate or the metal ethoxy alcoholates.

[Claim 3] Said metal methoxy alcoholate and a metal ethoxy alcoholate are the manufacture approach of the perovskite mold multiple

oxide according to claim 2 which are either ethylate or the PUROPI rates.

[Claim 4] Said organic solvent is the manufacture approach of the perovskite mold multiple oxide according to claim 1 to 3 which is either of hydrocarbons, alcohols, ketones, and ester.

[Claim 5] Said organic solvent is the manufacture approach of the perovskite mold multiple oxide according to claim 4 which are a xylene, toluene, or the benzene.

[Claim 6] The water solution of the salt of said noble-metals element B' is the manufacture approach of the perovskite mold multiple oxide according to claim 1 to 5 which are a nitrate, a chloride, a dinitrodiammine nitrate, a hexa ammine chloride, a hexa chloro acid hydrate, or the potassium-cyanide salts.

[Claim 7] The manufacture approach of a perovskite mold multiple oxide according to claim 1 to 6 that the burning temperature which obtains a perovskite mold multiple oxide from a precursor is 500-600 degrees C.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention is excellent in the purification capacity of a carbon monoxide (CO), a hydrocarbon (HC), and nitrogen oxide (NOx), and relates to the approach of manufacturing the perovskite mold multiple oxide used as catalysts for combustion, such as a catalyst for exhaust gas purification, and natural gas, etc.

[0002]

[Description of the Prior Art] As a three way component catalyst for exhaust gas purification, the precious metal catalyst which supported noble metals, such as Pt, Rh, and Pd, is put in practical use by alumina support, and it is widely used for it. Moreover, utilization is expected as a cheap three way component catalyst for exhaust gas purification with which the catalyst which made noble metals live together in the multiple oxide which has the perovskite type structure which consists of a rare earth metal, an alkaline earth metal, and transition metals purifies CO, HC, and NOx (refer to JP,59-87046,A, JP,60-82138,A, and JP,1-168343,A).

[0003] With these catalysts, after noble metals, such as Pd, have been distributed by the detailed perovskite mold multiple oxide front face, it is supported. However, after the noble-metals element has been supported by the front face of a perovskite mold multiple oxide, while continuing being used at an elevated temperature, a noble-metals element serves as floc, degree of dispersion of a noble-metals element becomes small, and properties, such as catalytic activity, tend to deteriorate.

[0004] Then, in order to make the degree of dispersion of a noble-metals element increase and to raise catalytic activity etc., the method of incorporating a noble-metals element in the crystal lattice of perovskite type structure is proposed. The water solution which dissolved the salt and citric acid of the metallic element which constitutes the perovskite mold multiple oxide containing a noble-metals element as the one approach is prepared. After forming the complex of a metallic element and a citric acid by drying the water solution, The complex is heated at 350 degrees C or more in a vacuum or inert gas, a temporary baking object is formed, and a perovskite mold multiple oxide is formed by calcinating it in an oxidizing atmosphere (refer to JP,6-100319,A).

[0005]

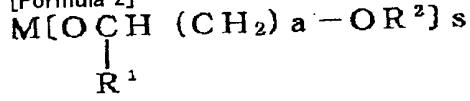
[Problem(s) to be Solved by the Invention] Although it is for the invention in this application to make degree of dispersion of a noble-metals element increase by putting in a noble-metals element into the crystal lattice of perovskite type structure as well as the approach proposed by JP,6-100319,A, and raise properties, such as catalytic activity, it aims at offering a different option from the approach.

[0006]

[Means for Solving the Problem] The manufacture approach of this invention is $O(B(A1-xA'x)1-yB'y)$ 3 (among a formula). At least one sort in La, Nd, and Pr and A' A At least one sort in Ce, Mg, calcium, Sr, Ba, and Y, B — Co, Mn, Fe, nickel, Cr, Cu, and Zn — inner at least one sort At least one sort in the noble-metals element with which B' consists of Ru, Rh, Pd, Os, Ir, and Pt, $0 < x < 0.9$ and $0.01 < y < 0.2$ — it is — among the metallic elements which constitute the perovskite mold multiple oxide shown What dissolved the metal alkoxy alcoholate of the metallic element except noble-metals element B' in the organic solvent, and was used as the mixed alkoxy alcoholate solution The process which removes an organic solvent and moisture and forms the precursor of a perovskite mold multiple oxide after hydrolyzing with the water solution of the salt of noble-metals element B' which constitutes a perovskite mold multiple oxide, The process which calcinates the precursor at 500-600 degrees C preferably, and uses it as a perovskite mold multiple oxide 500-800 degrees C among an oxidizing atmosphere is included.

[0007] The compound shown by the following formula as a metal alkoxy alcoholate can be used.

[Formula 2]



the inside of a formula, and M — the metal of the above-mentioned A, A', or the B, and R1 — a hydrogen atom or a low-grade alkyl group — in R2, a low-grade alkyl group and a show the integer of 1-3, and s shows the integer of 2-3, respectively. As for a metal alkoxy alcoholate, it is desirable that they are either a metal methoxy alcoholate or the metal ethoxy alcoholates also in it. As for the metal methoxy alcoholate and a metal ethoxy alcoholate, it is desirable that they are either ethylate or the PUROPI rates.

[0008] Moreover, it can use, without being limited as an organic solvent, especially if metal alkoxy alcoholates may be dissolved. If hydrocarbons, alcohols, ketones, and ester are specifically mentioned as such an organic solvent and solubility and operability are taken into consideration, aromatic hydrocarbon, such as a xylene, toluene, and benzene, will be used preferably. Although it is desirable that they are a nitrate, a chloride, a dinitrodiammine nitrate, a hexa ammine chloride, a hexa chloro acid hydrate, or the potassium-cyanide salts as for the water solution of the salt of noble-metals element B', it is not limited to it.

[0009]

[Function] Since a noble-metals element is difficult to make it an alkoxy alcoholate, it is made a water solution as a water-soluble salt, and other metallic elements are dissolved in an organic solvent as an alkoxy alcoholate. If both are mixed and agitated and an organic solvent and moisture are removed, the metallic element which constitutes a perovskite mold multiple oxide will serve as a precursor mixed to homogeneity. By calcinating the precursor in oxidizing atmospheres, such as atmospheric air, the perovskite mold multiple oxide with which noble metals were incorporated by the crystal lattice is obtained. In order to form a perovskite mold multiple oxide crystal, to calcinate above 500 degrees C is required. By the manufacture approach of this invention, at least 600 degrees C or less can be calcinated. If burning temperature is made low with 500-600 degrees C, it will become advantageous also from the field of a manufacturing facility.

[0010]

[Example]

[Example 1)

La — the following are prepared 0.9 Ce as an alkoxy alcoholate of metallic elements other than a 0.1Fe0.57Co0.38Pd0.05O₃ noble-metals element.

Lanthanum ethoxy ethylate 36.6g (0.09 mols)

La₃ (OC₂H₄OC₂H₅) Cerium ethoxy ethylate 4.1g (0.01 mols)Ce₃ (OC₂H₄OC₂H₅) Iron ethoxy ethylate 18.4g (0.057 mols)Fe₃ (OC₂H₄OC₂H₅) Cobalt ethoxy ethylate 9.0g (0.038 mols)

Co (OC₂H₄OC₂H₅)₂ — these metal alkoxy alcoholates were put into the round bottom flask of 500ml capacity, as an organic solvent, toluene 200ml was added, was agitated and dissolved, and it considered as the mixed alkoxy alcoholate solution.

[0011] On the other hand, the water solution which added 100ml of deionized water to 12.1g (Pd part 4.4wt(s)% (equivalent to 0.53g and 0.005 mols at Pd conversion) of palladium nitrate solutions as a water solution of a noble-metals salt was prepared. It was gradually dropped under the room temperature into the previous mixed alkoxy alcoholate solution, having palladium nitrate poured this [it for about 15 minutes. Brown precipitation generates immediately by dropping of a palladium nitrate water solution, and it becomes viscosity gradually. After agitating the solution under a room temperature for 2 hours, moisture and the toluene of an organic solvent were distilled off out of the system of reaction under reduced pressure, and the precursor of a dark-brown LaCeFeCoPd oxide was obtained.

[0012] After moving the viscous object of this precursor to the petri dish and carrying out draught drying at 60 degrees C for 24 hours, among air, it heat-treated at 600 degrees C with the electric furnace for 2 hours, and dark-brown powder was obtained. The powder was the perovskite mold single crystal phase of the result of the powder X diffraction shown in drawing 1 to La_{0.9}Ce_{0.1}Fe_{0.57}Co_{0.38}Pd_{0.05}O₃, and specific surface area was 30m²/g.

[0013] (Example 2)

La — the following are prepared 0.9 Ce as an alkoxy alcoholate of metallic elements other than a 0.1Mn0.57Co0.38Pd0.05O₃ noble-metals element.

Lanthanum ethoxy ethylate 36.6g (0.09 mols)

La₃ (OC₂H₄OC₂H₅) Cerium ethoxy ethylate 4.1g (0.01 mols)Ce₃ (OC₂H₄OC₂H₅) Manganese ethoxy ethylate 13.3g (0.057 mols)Mn₂ (OC₂H₄OC₂H₅) Cobalt ethoxy ethylate 9.0g (0.038 mols)

Co (OC₂H₄OC₂H₅)₂ — these metal alkoxy alcoholates were put into the round bottom flask of 500ml capacity, as an organic solvent, kylene 200ml was added, was agitated and dissolved, and it considered as the mixed alkoxy alcoholate solution.

[0014] The water solution which added 100ml of deionized water to 12.1g (Pd part 4.4wt(s)% (equivalent to 0.53g and 0.005 mols at Pd conversion) of palladium nitrate solutions as a water solution of a noble-metals salt was prepared like the example 1. The precursor of a dark-brown LaCeMnCoPd oxide was obtained from this mixed alkoxy alcoholate solution and a palladium nitrate water solution by the same approach as an example 1, it was heat-treated on the same conditions as an example 1, and dark-brown powder was obtained. The powder was the perovskite mold single crystal phase of the result of the powder X diffraction shown in drawing 2 to La_{0.9}Ce_{0.1}Mn_{0.57}Co_{0.38}Pd_{0.05}O₃, and specific surface area was 36m²/g.

[0015] (Example 3)

Nd — the following are prepared 0.6 calcium as an alkoxy alcoholate of metallic elements other than a 0.4Fe0.52Mn0.36Pd0.12O₃ noble-metals element.

Neodymium ethoxy ethylate 24.7g (0.06 mols)

Nd₃ (OC₂H₄OC₂H₅) Calcium ethoxy ethylate 8.7g (0.04 mols)Ca₂ (OC₂H₄OC₂H₅) Iron ethoxy ethylate 16.8g (0.052 mols)Fe₃ (OC₂H₄OC₂H₅) Manganese ethoxy ethylate 8.4g (0.036 mols)

Like Mn(OC₂H₄OC₂H₅)₂ example 1, these metal alkoxy alcoholates were put into the round bottom flask of 500ml capacity, as an organic solvent, toluene 200ml was added, was agitated and dissolved, and it considered as the mixed alkoxy alcoholate solution.

[0016] The water solution which added 100ml of deionized water to 29.0g (Pd part 4.4wt(s)% (equivalent to 1.27g and 0.012 mols at Pd conversion) of palladium nitrate solutions as a water solution of a noble-metals salt was prepared. The precursor of a dark-brown NdCaFeMnPd oxide was obtained from this mixed alkoxy alcoholate solution and a palladium nitrate water solution by the same approach as an example 1, it was heat-treated on the same conditions as an example 1, and dark-brown powder was obtained. The powder was the perovskite mold single crystal phase of Nd_{0.6}Ca_{0.4}Fe_{0.52}Mn_{0.36}Pd_{0.12}O₃, and specific surface area was 32m²/g.

[0017] (Example 4)

Pr — the following are prepared as an alkoxy alcoholate of metallic elements other than a 0.8Sr0.2Mn0.9Pd0.1O₃ noble-metals element.

Praseodymium methoxy ethylate 29.3g (0.08 mols)

Pr₃(OC₂H₄OCH₃) Strontium methoxy ethylate 4.8g (0.02 mols)

Sr₂(OC₂H₄OCH₃) Manganese methoxy ethylate 18.5g (0.09 mols)

Mn₂(OC₂H₄OCH₃) [0018] Like the example 1, these metal alkoxy alcoholates were put into the round bottom flask of 500ml capacity, as an organic solvent, toluene 200ml was added, was agitated and dissolved, and it considered as the mixed alkoxy alcoholate solution. The water solution which added 100ml of deionized water to 24.2g (Pd part 4.4wt(s)%)(equivalent to 1.06g and 0.01 mols at Pd conversion) of palladium nitrate solutions as a water solution of a noble-metals salt was prepared.

[0019] The precursor of a dark-brown PrSrMnPd oxide was obtained from this mixed alkoxy alcoholate solution and a palladium nitrate water solution by the same approach as an example 1, it was heat-treated on the same conditions as an example 1, and dark-brown powder was obtained. The powder was the perovskite mold single crystal phase of Pr_{0.8}Sr_{0.2}Mn_{0.9}Pd_{0.1}O₃, and specific surface area was 29m²/g.

[0020] (Example 5)

La_{0.2}Ba_{0.7}Y — the following are prepared as an alkoxy alcoholate of metallic elements other than a 0.1Cu0.48Cr0.48Pt0.04O₃ noble-metals element.

Lanthanum ethoxy ethylate 8.1g (0.02 mols)

La₃(OC₂H₄OC₂H₅) Barium ethoxy ethylate 22.1g (0.07 mols)

Ba₂(OC₂H₄OC₂H₅) Yttrium ethoxy ethylate 3.6g (0.01 mols)

Y(OC₂H₄OC₂H₅)₃ Copper ethoxy ethylate 11.6g (0.048 mols)

Cu₂(OC₂H₄OC₂H₅) Chromium ethoxy ethylate 15.3g (0.048 mols)

Cr₃(OC₂H₄OC₂H₅) [0021] Like the example 1, these metal alkoxy alcoholates were put into the round bottom flask of 500ml capacity, as an organic solvent, toluene 200ml was added, was agitated and dissolved, and it considered as the mixed alkoxy alcoholate solution.

The water solution which added 100ml of deionized water to 9.2g (Pt part 8.5wt(s)%)(equivalent to 0.78g and 0.004 mols at Pt conversion) of dinitrodiimmine platinum nitric-acid solutions as a water solution of a noble-metals salt was prepared.

[0022] The precursor of a dark-brown LaBaYC_uCr_{Pt} oxide was obtained from this mixed alkoxy alcoholate solution and a platinum-salts water solution by the same approach as an example 1, it was heat-treated on the same conditions as an example 1, and dark-brown powder was obtained. The powder was the perovskite mold single crystal phase of La_{0.2}Ba_{0.7}Y_{0.1}Cu_{0.48}Cr_{0.48}Pt_{0.04}O₃, and specific surface area was 26m²/g.

[0023] (Example 6)

La — the following are prepared 0.8 Ba as an alkoxy alcoholate of metallic elements other than a 0.2nickel0.48Co0.50Rh0.02O₃ noble-metals element.

Lanthanum-1-methoxy-2-PUROPI rate 32.5g (0.08 mols)

La₃(OCH(CH₃)CH₂OCH₃) Barium-1-methoxy-2-PUROPI rate 6.3g (0.02 mols)

Ba₂(OCH(CH₃)CH₂OCH₃) Nickel-1-methoxy-2-PUROPI rate 11.4g (0.048 mols)

Nickel₂(OCH(CH₃)CH₂OCH₃) Cobalt-1-methoxy-2-PUROPI rate 11.9g (0.050 mols)

Co₂(OCH(CH₃)CH₂OCH₃) [0024] Like the example 1, these metal alkoxy alcoholates were put into the round bottom flask of 500ml capacity, as an organic solvent, toluene 200ml was added, was agitated and dissolved, and it considered as the mixed alkoxy alcoholate solution. The water solution which added 100ml of deionized water to 4.69g (Rh part 4.478wt(s)%)(equivalent to 0.21g and 0.002 mols at Rh conversion) of nitric-acid rhodium solutions as a water solution of a noble-metals salt was prepared.

[0025] The precursor of a dark-brown LaBaNiCoRh oxide was obtained from this mixed alkoxy alcoholate solution and a nitric-acid rhodium water solution by the same approach as an example 1, it was heat-treated on the same conditions as an example 1, and dark-brown powder was obtained. The powder was the perovskite mold single crystal phase of La_{0.8}Ba_{0.2}nickel_{0.48}Co_{0.50}Rh_{0.02}O₃, and specific surface area was 27m²/g.

[0026] (Example 7)

La — the following are prepared 0.9 Ce as an alkoxy alcoholate of metallic elements other than a 0.1Co0.90Pt0.05Ru0.05O₃ noble-metals element.

Lanthanum ethoxy ethylate 36.6g (0.09 mols)

La₃(OC₂H₄OC₂H₅) Cerium ethoxy ethylate 4.1g (0.01 mols)

Ce₃(OC₂H₄OC₂H₅) [0027] Like the example 1, these metal alkoxy alcoholates were put into the round bottom flask of 500ml capacity, as an organic solvent, toluene 200ml was added, was agitated and dissolved, and it considered as the mixed alkoxy alcoholate solution.

The water solution which added 100ml of deionized water to 11.5g (Pt part 8.5wt(s)%)(equivalent to 0.98g and 0.005 mols at Pt conversion) of dinitrodiimmine platinum nitric-acid solutions and 13.0g (Ru part 3.930wt(s)%)(equivalent to 0.51g and 0.005 mols at Ru conversion) of nitric-acid ruthenium solutions as a water solution of a noble-metals salt was prepared.

[0028] The precursor of a dark-brown LaCeCoPtRu oxide was obtained from the mixed water solution of this mixed alkoxy alcoholate solution, platinum salts, and a ruthenium salt by the same approach as an example 1, it was heat-treated on the same conditions as an example 1, and dark-brown powder was obtained. The powder was the perovskite mold single crystal phase of La_{0.9}Ce_{0.1}Co_{0.90}Pt_{0.05}Ru_{0.05}O₃, and specific surface area was 23m²/g.

[0029] ((a) The example of a comparison)

The example of La_{0.9}Ce_{0.1}Fe_{0.57}Co_{0.38}Pd_{0.05}O₃ comparison is an example in which the perovskite mold multiple oxide which contains a noble-metals element with a coprecipitation method was formed. The following were prepared as configuration metal salts other than noble metals.

Lanthanum nitrate 39.0g (0.09 mols)

La(NO₃)₃·6H₂O Cerium nitrate 4.3g (0.01 mols)

Ce(NO₃)₃·6H₂O Ferric nitrate 23.0g (0.057 mols)

Fe(NO₃)₃·6H₂O Cobalt nitrate 11.1g (0.038 mols)

Co(NO₃)₂·6H₂O [0030] These metal salts were put into the beaker of 1000ml capacity, and 300ml of deionization water was added, and it agitated and dissolved and considered as the mixed water solution. 12.1g (Pd part 4.4wt(s)% (equivalent to 0.53g and 0.005 mols at Pd conversion) of palladium nitrate solutions was added to the water solution, and it agitated further and mixed. [0031] 500ml of water solutions which dissolved 35g of sodium carbonates in the mixed water solution was dropped as a neutralization coprecipitator, and the coprecipitate was obtained. The vacuum drying was carried out, after rinsing the coprecipitate enough and filtering it. After calcinating this in 3-hour atmospheric air at 600 degrees C, the powder of La_{0.9}Ce_{0.1}Fe_{0.57}Co_{0.38}Pd_{0.05}O₃ of the presentation which grinds, calcinates in 5-hour atmospheric air at 800 degrees C after that, grinds further, and is equivalent to an example 1 was created. The specific surface area after grinding was 29m²/g.

[0032] ((b) The example of a comparison)

La_{0.8} — the following were prepared as configuration metal salts other than Ba_{0.2}Ni_{0.48}Co_{0.50}Rh_{0.02}O₃ noble metals.

Lanthanum nitrate 34.7g (0.08 mols)

La(NO₃)₃·6H₂O Barium nitrate 5.2g (0.02 mols)

Ba(NO₃)₂·6H₂O Nickel nitrate 14.0g (0.048 mols)

Nickel(NO₃)₂·6H₂O Cobalt nitrate 14.6g (0.05 mols)

Co(NO₃)₂·6H₂O [0033] Replacing with the palladium nitrate, others created the powder of La_{0.8}Ba_{0.2}Ni_{0.48}Co_{0.50}Rh_{0.02}O₃ of the presentation which is equivalent to an example 6 with the same actuation as the example a of a comparison using 4.69g (Rh part 4.478wt(s)% (equivalent to 0.21g and 0.002 mols at Rh conversion) of nitric-acid rhodium solutions. The specific surface area after grinding of the powder was 24m²/g.

[0034] ((c) The example of a comparison)

La_{0.9} — the following were prepared as configuration metal salts other than Ce_{0.1}Co_{0.90}Pt_{0.05}Ru_{0.05}O₃ noble metals.

Lanthanum nitrate 39.0g (0.09 mols)

La(NO₃)₃·6H₂O Cerium nitrate 4.3g (0.01 mols)

Ce(NO₃)₃·6H₂O Cobalt nitrate 26.2g (0.09 mols)

Co(NO₃)₂·6H₂O [0035] Replacing with the palladium nitrate, others created the powder of La_{0.9}Ce_{0.1}Co_{0.90}Pt_{0.05}Ru_{0.05}O₃ of the presentation which is equivalent to an example 7 with the same actuation as the example a of a comparison using 11.5g (Pt part 8.5wt(s)% (equivalent to 0.98g and 0.005 mols at Pt conversion) of dinitrodiammime platinum nitric-acid solutions, and 13.0g (Ru part 3.930wt(s)% (equivalent to 0.51g and 0.005 mols at Ru conversion) of nitric-acid ruthenium solutions. The specific surface area after grinding of the powder was 26m²/g.

[0036] The powder obtained by examples 1-7 and example a-c of a comparison added deionized water separately, respectively, made it the slurry, and after it added and agitated the ceria sol (being the product of Taki Chemical Co., Ltd. need RARU W-10) at a rate of 10g to 20g of each fine particles further, it was applied to honeycomb-like cordierite support (400 cels / inch²). After drying it, it calcinated at 300 degrees C in atmospheric air for 3 hours, and the sample for a test was obtained. The die length of the honeycomb size of support is 50mm for the diameter of 30mm.

[0037] (Durability test) Following rich gas and lean gas were switched every 5 seconds, it repeated at 900 degrees C for 30 minutes, the cycle of 30 minutes was repeated 50 times (50 hours) at 750 degrees C, and the durability test was performed. Space velocity (SV) of the gas stream which passes along a catalyst was made into 30,000-/time amount.

[0038] Rich gas Lean gas CO 2.6 % 0.7 % HC (C1 conversion concentration) 0.19% 0.19% H₂ 0.87% 0.23% CO₂ 8 % 8 % NO 0.17% 0.17% O₂ 0.74% 1.89% H₂O steam 10% 10 % N₂ Remainder As for the items of Remainder HC, C₃H₆ were [C₃H₈] 0.04% 0.15%.

[0039] (Evaluation of catalytic activity) The temperature up of a sink and the gas was heated and carried out to the honeycomb sample for a test, switching above-mentioned rich gas and lean gas for every second. The programming rate was considered as a part for 20-degree-C/, and measured and controlled gas ** near a catalyst inlet port. Measurement of catalytic activity was performed in front of a durability test and in the back. Space velocity (SV) of the gas stream which passes along a catalyst was made into 30,000-/time amount. The rate of purification of HC and CO in 350 degrees C (%) is collectively shown in Table 1.

[0040]

[Table 1]

	HC		CO	
	初期	耐久試験	初期	耐久試験後
実施例 1	9 7	9 4	9 8	9 8
実施例 2	9 9	9 7	9 9	9 8
実施例 3	9 6	9 6	9 7	9 6
実施例 4	9 7	9 6	9 7	9 7
実施例 5	8 0	7 8	8 4	8 4
実施例 6	9 1	8 8	9 6	9 4
実施例 7	9 9	9 1	9 9	9 9
比較例 a	8 2	6 3	9 1	8 9
比較例 b	7 6	4 8	9 3	8 2
比較例 c	8 3	6 7	9 6	9 2

[0041] The catalytic activity over HC excels the example of a comparison in the example after durability also in the initial state. A large difference is not seen about CO. Moreover, if the rate of purification of HC and CO after an initial state and durability is compared, there is little degradation in the example and degradation in the example of a comparison has appeared greatly especially in HC. Thus, also in endurance, the catalyst by the approach of this invention is superior to the thing of the example of a comparison.

[0042] Although the test result to nitrogen oxides NOx is not shown, this is for depending for the rate of purification of NOx on the class of noble-metals element greatly rather than the manufacture approach. When using palladium as a noble-metals element, the rate of purification of NOx brings the result of having excelled most. Also to NOx, the perovskite mold multiple oxide by this invention is effective, and acts as a three way component catalyst.

[0043]
[Effect of the Invention] The perovskite mold multiple oxide manufactured by the approach of this invention serves as a catalyst which the noble-metals element went into the crystal lattice, was excellent in catalytic activity, and was excellent also in endurance.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the chart Fig. showing the X diffraction result of the perovskite mold multiple oxide powder manufactured according to an example 1.

[Drawing 2] It is the chart Fig. showing the X diffraction result of the perovskite mold multiple oxide powder manufactured according to an example 2.

[Translation done.]

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